

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66655 A1

(51) International Patent Classification⁷: C09D 4/00,
183/08, C08J 7/04

(21) International Application Number: PCT/US01/05573

(22) International Filing Date: 21 February 2001 (21.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/518,739 3 March 2000 (03.03.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/66655 A1

(54) Title: BARRIER COATING COMPOSITIONS FROM AMINO FUNCTIONAL SILANES AND PHENOLIC COMPOUNDS

(57) Abstract: The reaction products of amino functional silanes and phenolic compounds provide improved barrier coating compositions. These compositions are particularly useful to reduce the diffusion of gases through organic polymer packaging materials, such as polypropylene, even in conditions involving high relative humidity.

BARRIER COATING COMPOSITIONS FROM AMINO FUNCTIONAL SILANES AND PHENOLIC COMPOUNDS

Field of the Invention

5 The present invention relates to coating compositions having barrier properties which are useful in packaging applications. The coating compositions of this invention are formed by the reaction of amino functional silanes with phenolic compounds, and are particularly useful to reduce the diffusion of gases through organic polymer based packaging materials.

Background of the Invention

10 Organic polymers, such as polypropylene and polyethylene terephthalate, have gained wide acceptance in the packaging industry because of their inherent advantages over conventional materials such as glass. However, a need exists to improve the barrier properties of organic polymer films for various packaging applications. More particularly, improvements are sought to prevent the loss of gaseous, oil, and flavor components of compositions packaged with organic polymer film substrates.

15 Coating compositions containing silane compounds are known to improve the gas, oil, and flavor barrier performance of organic polymer film substrates, for example as described in PCT/BE98/00006, the corresponding US equivalent of which is US Serial No. 09/341253. Moreover, the adhesion of the coating to the film surface, as well as the improved barrier characteristics provided by the silane coating, are greatly enhanced by exposing the coated film to electron beam radiation.

20 Useful barrier compositions are described in U.S. Patent No. 5,215,822, which teaches a methanol solution of a vinyl benzyl amine silane, itaconic acid, and water; coating this solution on a corona treated low density polyethylene film, drying, and then subjecting the coated film to electron beam radiation to graft the coating to the film surface and further improve the barrier properties of the silane coating. However, while this coating gives excellent gas barrier properties at low to moderate relative humidity values, the gas permeability increases drastically at very high relative humidity values.

25 U.S. Patent No. 5,434,007 teaches a silane resin coated on a plastic film, where the silane resin is composed of a monofunctional acrylate and an amino functional silane.

30 U.S. Patent Nos. 5,260,350 and 5,374,483 relate to a silicone coating composition which, when cured on a solid substrate either by ultraviolet or electron beam radiation, provides a transparent abrasion resistant coating firmly adhered thereon. The silicone coating is prepared

by reacting at least one multifunctional acrylate monomer with an amino-organofunctional silane, mixing the modified silane with at least one acrylic monomer and thereafter adding colloidal silica.

JP (Kokai) publication 7-18221 published on January 20, 1995 teaches a surface treatment composition for gas barrier comprising an amino functional silane and a compound having an aromatic ring or hydrogenated ring.

These coatings represent a significant advance in the art. However, it has been observed that while the barrier properties of the prior art coatings are excellent in environments at relative humidities of 80% or less, their performance suffers significantly at relative humidities of 90% or more.

The present inventor has surprisingly discovered that the reaction products of an amino functional silane and a phenolic compound give excellent gas barrier properties at low to moderate relative humidity values, as well as excellent gas barrier properties at very high relative humidity values of 90% or more.

Coating compositions for improving barrier properties of organic polymer films based primarily on the reaction product of amino functional silanes and phenolic compounds heretofore are not known. Amino functional silanes are commonly used as surface treatments of silicate based materials (such as glass or silica) to enhance the adhesion of a wide variety of organic polymers. Examples of the type of organic polymers reacted with amino functional silane treated silicate materials includes phenol-formaldehyde polymers. Furthermore, the addition of phenolic compounds to phenol-formaldehyde resin coating compositions are known. In particular, US Patent No. 4,062,690 teaches a coating composition for glass fibers based on phenol-formaldehyde resins containing at least one monocyclic or polycyclic aromatic compound having at least three hydroxyl groups on the aromatic ring. While the '690 patent further teaches the treatment of the glass fibers with an amino functional silane, it does not specifically describe or suggest the reaction product of a amino functional silane with a non-resin phenolic compound is useful to improve the barrier properties of organic polymer films. Rather, the '690 teaches the necessity of mixing a phenolic compound in a phenol-formaldehyde resin to obtain a coating composition.

Silamines have been reacted with phenols to create curing agents for epoxide resins, as taught in US Patent No. 4,393,180. However, these silamines differ from the amino functional silanes of the present invention in that they do not contain an alkoxy group and have not been suggested for improving the barrier properties of organic polymer films.

Summary of the Invention

The present invention is directed to a composition, useful for improving the barrier properties of organic polymer films, prepared by reacting;

(A) an amino functional silane and

(B) a phenolic compound

to form a reaction product. The composition should be free of phenol-formaldehyde resole resin. The composition can be cured by further heating in the presence of moisture.

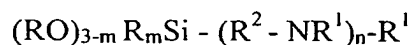
The present invention also teaches a method for preparing substrates with improved barrier properties by coating a variety of substrates used in packaging applications with the inventive compositions.

The substrates prepared by the method of the present invention show improved resistance of the substrate to transmission of gases and aromas there through. For example, a 30 micrometers uncoated biaxially oriented, corona treated polypropylene film is generally found to have a permeability to oxygen of 1200 cc/m²/day as measured according to ASTM D3985-81 at 90% relative humidity. With the preferred embodiments of the present invention, the oxygen transmission rate of the same film is reduced to less than 1 cc/m²/day as measured at 90% relative humidity. As used herein, the terminology "improved barrier" refers to a coating which can reduce oxygen transmission rate of the aforementioned un-coated polypropylene film from 1200 cc/m²/day to less than 100 cc/m²/day as measured at ASTM D3985-81 measured at 90% relative humidity.

Other advantages and aspects of the present invention will become better understood with reference to the following description and appended claims.

Detailed Description of the Invention

The amino functional silanes useful as component A) in the composition of the present invention are described by the formula;



wherein m is 0, 1 or 2, n is 1 - 3,

R is independently a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms,

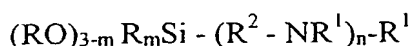
R¹ is independently a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an arylalkyl group, an acryl group, a methacryl group, or an alkylaryl group,

R^2 is independently selected from the group consisting of,

linear or branched alkylene groups having from 1 to 12 carbon atoms,
 arylene groups having from 6 to 12 carbon atoms,
 and linear or branched hydrocarbon groups having from 1 to 16 carbon
 atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or
 polyether group

The most preferred amino functional silanes useful for the present invention are N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, and aminopropyltriethoxysilane, and blends thereof.

For the purposes of the present invention, the above mentioned amino functional silane has the general formula;



wherein m is 0, 1 or 2, n is 1 - 3,

In the above formula, R^1 is a monovalent radical independently selected from the group consisting of hydrogen atoms; acryl, methacryl, alkyl groups having 1 to 18 carbon atoms, such as methyl, ethyl, propyl, isobutyl, hexyl, octyl, decyl, dodecyl and octadecyl; substituted alkyl having 1 to 18 carbon atoms, such as 3-chloropropyl and 3,3,3-trifluoropropyl; aryl having 6 to 16 carbon atoms, such as phenyl and naphthyl; substituted aryl having 6 to 30 carbon atoms, such as chlorophenyl, chlorotolyl and dichloroxylyl; arylalkyl having 7 to 9 carbon atoms, such as benzyl, phenethyl and 3-phenylpropyl; and alkylaryl having 7 to 16 carbon atoms, such as tolyl, xylyl, ethylphenyl and propyltolyl.

R^1 can also be an alkylene linking group which links two different nitrogen atoms together, thus forming a cyclic aminosilane. The alkylene linking group can also be an arylene group which is connected to the same nitrogen atom. The alkylene linking group will have at least 2 carbon atoms and as many as 12 carbon atoms.

R^2 is an organic connecting group which provides a separation of at least one carbon atom between the nitrogen atoms or the nitrogen and silicon atoms. Thus, R^2 can be an alkylene group having at least 1 carbon atom or an arylene group having at least 6 carbon atoms. Preferably, R^2 is selected from the group consisting of methylene, ethylene, propylene, butylene, isobutylene, trimethylene, tetramethylene, and hexamethylene.

In addition, R^2 can contain polar groups such as, linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester, amide, urea,

thiourea or polyether group. Specific examples of such groups include, those having the general formula $-\text{CH}_2\text{CH}(\text{OH})(\text{CH}_2)_x-$, $-\text{CH}_2\text{CH}(\text{OH})(\text{CH}_2)_x-\text{O}-(\text{CH}_2)_y-$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_y-$, $-\text{CH}_2\text{CH}_2\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_y-$, $-\text{CH}_2\text{CH}_2\text{C}(=\text{O})-\text{N}(\text{R})-(\text{CH}_2)_y-$, $-\text{C}(=\text{O})-\text{N}(\text{R})-(\text{CH}_2)_y-$, $-\text{C}(=\text{S})-\text{N}(\text{R})-(\text{CH}_2)_y-$, or where x and y are each integers from 1 to 12. The hydroxyl and ester groups are highly polar, and it is believed the polar nature of the groups improve barrier properties.

Examples of specific amine-containing groups include such structures as -
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NH}_2$, -
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, -
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$, $-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, -
 $\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Et}$, -
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Et})\text{H}$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NH}_2$ and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, inter alia, wherein Me and Et denote methyl and ethyl, respectively. A specific example of an amine containing cyclic group is piperazine.

As used herein the term "amino functional silane" can mean a single species of the formula described above, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, or it can mean mixtures of one or more species of amino functional silanes, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and aminopropyltriethoxysilane.

The above described amino functional silanes can be prepared by methods known to those skilled in the art, and which are amply described in the chemical literature.

Component B) of our composition is a phenolic compound. One skilled in the art recognizes phenolic compounds to be any compound having a structure with at least one hydroxy group substituent on an aromatic ring. The inventor believes any phenolic compound will suffice for reaction with the amino functional silanes described above to form the compositions of this present invention. While not to be bound by any theory, the inventor believes the hydroxy group of the phenolic compound reacts with the alkoxy group of the amino functional silane, liberating alcohol (corresponding to the alkoxy group on the amino functional silane) and forming a complex. The complex unexpectedly provides unique physical properties that make them useful in the preparation of barrier coatings.

The phenolic compounds of this invention may be further substituted with a variety of chemical groups, such as hydrogen, alkyl, aryl, hydroxy, carboxylic acids, esters, thio, amino, amide, or nitro groups. Preferably, the phenolic compound has two or more hydroxy substituents on its aromatic ring structure.

The phenolic compounds may have one or several aromatic rings in its structure. When the phenolic compound contains polycyclic aromatic rings, the polycyclic aromatic structure is preferably chosen from the group consisting of naphthyl, anthryl, and phenanthryl derivatives. Preferred embodiments of a polycyclic aromatic phenolic compound are 1, 5 dihydroxynaphthalene and 2, 7 dihydroxynaphthalene.

Most preferably, the phenolic compound has one aromatic ring and contains several hydroxy substituents. A specific preferred embodiment is when the phenolic compound is 1, 2, 3, -trihydroxybenzene, commonly known as pyrogallol.

The components (A) and (B) of the present invention can be reacted together in a solvent. The solvent must wet the substrate and should not extend the drying time of the coating beyond what is commercially acceptable. The amount of solvent can range from about 1% to about 99%. Preferably the solvent is present from about 5 to about 95 parts by weight of the total composition, and most preferably is present from about 70 to about 80 parts by weight of the total composition. In general, alcohols serve as suitable solvents. Preferred solvents are methanol, ethanol, n-propanol, isopropanol, butanol, and 1-methoxy-2-propanol (available as "Dowanol PM" from the Dow Chemical Co., Midland, MI), with methanol as the most preferred.

The coating can be applied in any desired amount, however, it is preferred that the coating be applied in a thickness ranging from 0.05 micrometers to 15 micrometers, the preferred coating thickness range being from about 0.5 to about 7 micrometers. Coating thickness can be determined by Scanning Electron Microscopy or by the use of a profiler (Tencor P-1 Long Scan Profilometer, Tencor Instruments, Santa Clara, CA). The coating can be applied to the substrate by any conventional method, such as spray coating, roll coating, slot coating, meniscus coating, immersion coating, and direct, offset, and reverse gravure coating.

The coating can be disposed on a wide variety of substrates, including, but not limited to polyolefins, such as oriented polypropylene (OPP), cast polypropylene, polyethylene and polyethylene copolymers, polystyrene, polyesters, such as polyethylene terephthalate (PET), or polyethylene naphthalate (PEN), polyolefin copolymers, such as ethylene vinyl acetate, ethylene acrylic acid and ethylene vinyl alcohol (EVOH), polyvinylalcohol and copolymers thereof, polyamides, such as nylon, and nylon MXD6, polyimides, polyacrylonitrile, polyvinylchloride, polyvinyl dichloride, polyvinylidene chloride, and polyacrylates, ionomers, polysaccharides, such as regenerated cellulose, and silicone, such as rubbers or sealants, other natural or synthetic rubbers, glassine or clay coated paper, paper board or craft paper, and metallized polymer films

and vapor deposited metal oxide coated polymer films, such as AlO_x , SiO_x , or TiO_x .

The aforesaid substrates are likely to be in the form of a film or sheet, though this is not obligatory. The substrate may be a copolymer, a laminate, a coextruded, a blend, a coating or a combination of any of the substrates listed above according to the compatibility of the materials with each other. In addition, the substrate may be in the form of a rigid container made from materials such as polyethylene, polypropylene, polystyrene, polyamides, PET, EVOH, or laminates containing such materials.

The aforesaid substrates may also be pretreated prior to coating by corona treatment, plasma treatment, acid treatments and flame treatments, all of which are known in the art.

In addition, the compositions of the present invention can be used for a wide variety of packaging containers, such as pouches, tubes, bottles, vials, bag-in-boxes, stand-up pouches, gable top cartons, thermo-formed trays, brick-packs, boxes, cigarette packs and the like.

Of course, the present invention is not limited to just packaging applications, and may be used in any application wherein gas, or aroma barrier properties are desired, such as tires, buoyancy aides, inflatable devices generally, etc.

Any of the foregoing substrates may have a primer or primers applied thereon. The primers are applied to the substrates by methods known in the art such as spray coating, roll coating, slot coating, meniscus coating, immersion coating, and indirect, offset, and reverse gravure coating. Suitable primers include, but are not limited to carbodiimide, polyethylenimine, and silanes, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and aminopropyltriethoxysilane.

While the compositions of the present invention will form films at ambient conditions, optimum results are achieved by heat curing. Generally, the higher the temperature, the faster the coating will solidify. The upper limit to the heating is the temperature at which the substrate will undergo unacceptable distortion. Also, heating will accelerate the rate of hydrolysis of silicon/alkoxy groups and also the rate of condensation of the silicon bonded alkoxy groups with silicon bonded hydroxy groups to form silicon-oxygen-silicon groups. The composition may be dried at room temperature or in an oven at temperatures up to about 140°C , with temperatures of from about 60°C to about 120°C being preferred and temperatures of about 60°C to about 80°C being most preferred. Heating time is temperature and solvent dependent and the coating will reach tack free time in 1 to 10 seconds. The heating step serves to evaporate the solvent when used and accelerate the condensation reaction between Si-OH groups and SiOH/SiOR groups.

Various optional additives can be added to the composition to improve various properties. These additives may be added as desired and in any amount as long as they do not reduce the performance of the barrier coatings as illustrated herein. Examples of additives include additional additives as earlier described, antiblock and slip aides such as stearamide, oleamide or polar additives, such as epoxides, polyols, glycidols or polyamines, such as polyethylenimine, and other silanes may be added. Specifically excluded from the scope of the present invention are colloidal silicas and silanes or other molecules having four alkoxy or other hydrolyzable groups disposed on a single silicone or other organometalic atom, such as tetraethoxy silane, and the like. Wetting agents, such as a polyethoxylated alkyl phenols may also be added.

Specifically excluded from the compositions of the present invention are phenol-formaldehyde resins.

The foregoing specification describes only the preferred embodiment and the alternate embodiments of the invention. Other embodiments may be articulated as well. It is expected that others will perceive differences which while differing from the foregoing, do not depart from the spirit and scope of the invention herein described and claimed.

Examples

The following examples are presented to further illustrate this invention, but are not to be considered as limiting the invention, which is delineated in the appended claims.

Several amino functional silanes and phenolic compounds were combined at varying ratios in a solvent, the resulting solutions coated as a film onto plastic substrates, and then cured in an oven. All starting materials were obtained from various commercial sources, as detailed below.

The solvent employed in all examples was methanol, used as obtained from Fisher. The trimethoxysilylpropyl amine used was obtained as Siquist A1110 from Witco/OSi, (Greenwich, CT). The N-(2-amino ethyl)gamma aminopropyl trimethoxysilane used was Dow Corning® Z6020 (Midland, MI). The pentaerythritol tetraacrylate (PETA, SR 295) was obtained from Sartomer, (Exton, PA). The photoinitiator was Darocur 1173 [titanium bis(ethyl-3-oxobutanoato-O¹,O³)bis(2-propanolato)-]from CIBA additives (CIBA Additives Division, Tarrytown, NY). All phenolic compounds, and 1,4 cyclohexanediol, were obtained and used as received from the Aldrich Chemical Company (Milwaukee, WI).

The coating solutions were applied to either polypropylene or polyethylene terephthalate

plastic substrates utilizing a laboratory drawdown rod (from UV Supply Processes, Inc., Chicago, IL). The coated films were then dried and cured in an oven at 60°C for 10 minutes. The oxygen permeability values for each film were measured and recorded in units of cc/square meter per 24 hours (day), "dry" values being measured at 0% relative humidity and "wet" values at 90% relative humidity utilizing MOCON Oxtran 2/20 Series. The MOCON instruments were obtained from Modern Controls Corporation. Coating thickness was determined by the use of a profiler (Tencor P-1 Long Scan Profilometer, Tencor Instruments, Santa Clara, CA).

The polypropylene substrate was corona treated 30 micrometer thick oriented polypropylene film (hereafter referred to as OPP), obtained from UCB Films (product T217/30).

For comparison, the OPP base film had a permeability of about 1191 cc/square meter/day under dry conditions and 1238 cc/square meter/day under wet conditions. The polyethylene terephthalate (hereafter referred to as PET) film substrate was 48 gauge DuPont Mylar LBT2. For comparison, the PET base film had a permeability of 144 cc/m²/day under dry conditions and 123 cc/m²/day under wet conditions.

Example 1 -- A1110 alone on OPP

A solution of 3 g of A1110 and 7 g of methanol was prepared and this was coated on the substrate by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 63.1 cc dry and 1253 cc wet and the coating thickness was found to be 1.2 micrometers.

Example 2 -- Z6020 alone on OPP

A solution of 3 g of Z6020 and 7 g of methanol was prepared and this was coated on the substrate by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 21.7 cc dry and 1339 cc wet and the coating thickness was found to be 1.9 micrometers.

Example 3 -- A1110/pyrogallol (90:10wt) on OPP

A solution of 2.7 g of A1110 and 7 g of methanol was prepared and 0.3 g of pyrogallol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 317.8 cc dry and 219.5 cc wet and the coating thickness was found to be 1.7 micrometers.

Example 4 -- A1110/pyrogallol (70:30wt) on OPP

A solution of 2.1 g of A1110 and 7 g of methanol was prepared and 0.9 g of pyrogallol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be

157.4 cc dry and 0.3cc wet and the coating thickness was found to be 1.47 micrometers.

Example 5 – Z6020/pyrogallol (90:10wt) on OPP

A solution of 2.7 g of Z6020 and 7 g of methanol was prepared and 0.3 g of pyrogallol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 196.9 cc dry and 447.3 cc wet and the coating thickness was found to be 0.9 micrometers.

Example 6 -- Z6020/pyrogallol (70:30wt) on OPP

A solution of 2.1 g of Z6020 and 7g of methanol was prepared and 0.9 g of pyrogallol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 33.3 cc dry and 0.1 cc wet and the coating thickness was found to be 3.2 micrometers.

The barrier data results for the coatings of examples 1 - 6 on OPP are summarized in Table 1. No trihydroxybenzenes were added to Examples 1-2 to produce films that could be used as controls for comparison purposes. In Examples 3-4, pyrogallol was added to aminopropyl trimethoxysilane (A1110) in different weight ratios as indicated. In Examples 5-6, pyrogallol was added to N-(2-amino ethyl)gamma aminopropyl trimethoxysilane (Z6020) in different weight ratios as indicated. These results show the improvement in barrier properties of polypropylene films when coated with the reaction product of pyrogallol and an amino functional silane.

Table 1

Barrier Data: Examples 1-6 (amino functional silane + pyrogallol), on OPP

Example #	Silane	phenol type	Ratio silane/phenol wt	Thickness μ	OTR ¹ 0%RH cc/m ² /day	OTR 90%RH cc/m ² /day	OTR ² predicted ³ 3micrometers coating 0%RH cc/m ² /day	OTR ³ predicted ³ 3micrometers coating 90%RH cc/m ² /day
OPP	-	-	-	-	1191	1238	-	-
1	A1110	none	100:0	1.2	63.1	1253	26.1	OPP ⁴
3	A1110	pyrogallol	90:10	1.7	317.8	219.5	203.6	134.7
4	A1110	pyrogallol	70:30	1.47	157.4	0.3	82.7	0.15
2	Z6020	none	100:0	1.9	21.7	1339	13.84	OPP
5	Z6020	pyrogallol	90:10	0.9	196.9	447.3	66.8	179.6
6	Z6020	pyrogallol	70:30	3.2	33.3	0.1	35.45	0.11

where:

1: OTR is oxygen transmission rate or oxygen gas permeability

2: OTR_{predicted} was calculated by the use of the Generic Composite Permeability Eq: $T_i/P_t = T_s/P_s +$

T_c/P_c where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_i, P_i), substrate (T_s, P_s), & coating (T_c, P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 cc/m²/day at 0%RH.

- 3: same as 2 except that the permeability was measured to be 1238cc/m²/day as measured at 90%RH
- 4: Permeability expected is that provided by the base film OPP itself.

In the following examples 7 - 13, various phenolic compounds were combined with amino functional silanes and coated on OPP. In Example 7, hydroquinone was added to Silquest A1110 in the weight ratio indicated. In Examples 8-11, dihydroxynaphthalenes were added to Silquest A1110 in different weight ratios as indicated. In Example 12, hydroquinone was added to Z6020 in the weight ratio indicated. In Example 13, 1,5-dihydroxynaphthalene was added to Z6020 in the weight ratio indicated.

Example 7 -- A1110/hydroquinone (70:30wt) on OPP

A solution of 2.1 g of A1170 and 7 g of methanol was prepared and 0.9 g of hydroquinone was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 144.7 cc dry and 65.2 cc wet and the coating thickness was found to be 6.9 micrometers.

Example 8 -- A1110/1,5-dihydroxynaphthalene (70:30wt) on OPP

A solution of 2.1 g of A1170 and 7g of methanol was prepared and 0.9 g of 1,5-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 78.5 cc dry and 1.2 cc wet and the coating thickness was found to be 5.8 micrometers.

Example 9 -- A1110/1,5-dihydroxynaphthalene (50:50wt) on OPP

A solution of 1.5 g of A1170 and 7 g of methanol was prepared and 1.5 g of 1,5-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 72.4 cc dry and 1.3 cc wet and the coating thickness was found to be 4.4 micrometers.

Example 10 -- A1110/2,7-dihydroxynaphthalene (70:30wt) on OPP

A solution of 2.1 g of A1170 and 7 g of methanol was prepared and 0.9 g of 2,7-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability

was determined to be 47 cc dry and 2.1 cc wet and the coating thickness was found to be 7.7 micrometers.

Example 11 -- A1110/2,7-dihydroxynaphthalene (50:50wt) on OPP

5 A solution of 1.5 g of A1170 and 7 g of methanol was prepared and 1.5 g of 2,7-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 50.1 cc dry and 1.6 cc wet and the coating thickness was found to be 3.8 micrometers.

Example 12 -- Z6020/hydroquinone (70:30wt) on OPP

10 A solution of 2.1 g of Z6020 and 7 g of methanol was prepared and 0.9 g of hydroquinone was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 35.7 cc dry and 108.8 cc wet and the coating thickness was found to be 1.65 micrometers.

15 Example 13 -- Z6020/1,5-dihydroxynaphthalene (70:30wt) on OPP

A solution of 2.1g of Z6020 and 7 g of methanol was prepared and 0.9 g of 1,5-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 13.6 cc dry and 20 cc wet and the coating thickness was found to be 4.2 micrometers.

20 The results for examples 7 - 13, shown in Table 2, demonstrate that compositions resulting from the reaction of these amino functional silanes and phenolic compounds yield improved barrier coatings.

Table 2

Barrier Data: Examples 7-14 (aminosilane + dihydroxy-aromatics) on OPP

Example #	Silane	phenol type	Ratio silane/HB	Thickness	OTR ¹ 0%RH	OTR 90%RH	OTR ² predicted ² 3micrometers coating 0%RH	OTR ³ predicted ³ 3micrometers coating 90%RH
			wt	μ	Cc/m ² /day	cc/m ² /day	cc/m ² /day	cc/m ² /day
OPP	-	-	-	-	1191	1238	-	-
1	A1110	none	100:0	1.2	63.1	1253	26.1	OPP ⁴
7	A1110	hydroquinone	70:30	6.9	144.7	65.2	287.4	140.4
8	A1110	1,5-DHN ⁵	70:30	5.8	78.5	1.2	142.3	2.3
9	A1110	1,5-DHN	50:50	4.4	72.4	1.3	103.3	1.9
10	A1110	2,7-DHN	70:30	7.7	47	2.1	113.6	5.4
11	A1110	2,7-DHN	50:50	3.8	50.1	1.6	62.8	2
2	Z6020	none	100:0	1.9	21.7	1339	13.84	OPP
12	Z6020	hydroquinone	70:30	1.65	35.7	108.8	19.9	62.3
13	Z6020	1,5-DHN	70:30	4.2	13.6	20	19	27.8

where:

- 1: OTR is oxygen transmission rate or oxygen gas permeability
- 2: OTR_{predicted} was calculated by the use of the Generic Composite Permeability Eqt: $T_t/P_t = T_s/P_s + T_c/P_c$ where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_t , P_t), substrate (T_s , P_s), & coating (T_c , P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 cc/m²/day at 0%RH.
- 3: same as 2 except that the permeability was measured to be 1238cc/m²/day as measured at 90%RH
- 4: Permeability expected is that provided by the base film OPP itself
- 5: DHN is dihydroxynaphthalene

In Example 14, a solution of Z6020 reacted with 1,5-dihydroxynaphthalene (in 70:30wt) in methanol was evaluated on PET.

Example 14 -- Z6020 /1,5-dihydroxynaphthalene (70:30wt) on PET

A solution of 2.14 kg of Z6020 and 11.9 kg of methanol was prepared, then 0.9 kg of 1,5-dihydroxynaphthalene was added with stirring. This was coated on the substrate after 2 hours of mixing by the use of a # 14 drawdown rod. After coating, drying and curing, the permeability was determined to be 6.2 cc dry and 26 cc wet and the coating thickness was found to be 0.37 micrometers.

The results from example 14, summarized in Table 3, show the improvements in the barrier properties when this composition is coated on PET.

Table 3

Example #	Silane	phenol type	Ratio silane/phenol wt	Thickness μ	OTR ¹ 0%RH cc/m ² /day	OTR 90%RH cc/m ² /day	OTR _{predicted} ² 3micrometers coating 0%RH cc/m ² /day	OTR _{predicted} ³ 3micrometers coating 90%RH cc/m ² /day
PET	-	-	-	-	144	123	-	-
14	Z6020	1,5-DHN ⁴	70:30	0.37	6.2	26	0.79	3.94

where:

- 1: OTR is oxygen transmission rate or oxygen gas permeability
- 2: OTR_{predicted} was calculated by the use of the Generic Composite Permeability Eq: $T_t/P_t = T_s/P_s + T_c/P_c$ where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_t , P_t), substrate (T_s , P_s), & coating (T_c , P_c). The substrate PET was measured to be 12 micrometers thick and have an OTR of 144cc/m²/day as measured at 0%RH.
- 3: same as 2 except that the permeability was measured to be 123 cc/m²/day at 90%RH
- 4: DHN is dihydroxynaphthalene

In Examples 15-19, barrier coating compositions prepared from amino functional silanes and monohydroxy-benzene and monohydroxy-naphthalene were evaluated on OPP. In Examples 15-17, monohydroxy- containing aromatics were added to Silquest A1110 in different weight ratios as indicated. In Examples 18-19, monohydroxy- containing aromatics were added to Z6020 in different weight ratios as indicated.

Example 15 -- A1110/phenol (90:10wt) on OPP

A solution of 2.7 g of A1110 and 7 g of methanol was prepared and 0.3 g of phenol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 34.4 cc dry and 1238.6 cc wet and the coating thickness was found to be 2.95 micrometers.

Example 16 -- A1110/phenol (70:30wt) on OPP

A solution of 2.1 g of A1110 and 7 g of methanol was prepared and 0.9 g of phenol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 71 cc dry and 1059.3 cc wet and the coating thickness was found to be 1.9 micrometers.

Example 17 -- A1110/2-naphthol (70:30wt) on OPP

A solution of 2.1 g of A1110 and 7 g of methanol was prepared and 0.9 g of 2-naphthol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be

148.1 cc dry and 404 cc wet and the coating thickness was found to be 2.9 micrometers.

Example 18 -- Z6020/phenol (70:30wt) on OPP

A solution of 2.1 g of Z6020 and 7 g of methanol was prepared and 0.9 g of phenol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 149 cc dry and 1302.3 cc wet and the coating thickness was found to be 2.4 micrometers.

Example 19 -- Z6020/2-naphthol (70:30wt) on OPP

A solution of 2.1 g of Z6020 and 7 g of methanol was prepared and 0.9 g of 2-naphthol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 39.4 cc dry and 102 cc wet and the coating thickness was found to be 3.1 micrometers.

The results for examples 15 - 19, shown in Table 4, demonstrate that monohydroxy aromatics when combined with aminosilanes, provide barrier coatings.

Table 4

Barrier Data: Examples 15-19 (aminosilanes + monohydroxy-aromatics) on OPP

Example #	Silane	phenol type	Ratio silane/phenol	Thickness μ	OTR ¹ 0%RH $cc/m^2/day$	OTR 90%RH $cc/m^2/day$	OTR ² predicted 3micrometers coating 0%RH $cc/m^2/day$	OTR ³ predicted 3micrometers coating 90%RH $cc/m^2/day$
OPP	-	-	-	-	1191	1238	-	-
1	A1110	none	100:0	1.2	63.1	1253	26.1	OPP ⁴
15	A1110	phenol	90:10	2.95	34.4	1238	33.8	OPP
16	A1110	phenol	70:30	1.9	71	1059.3	46	977.6
17	A1110	2-naphthol	70:30	2.9	148.1	404	143	394.8
2	Z6020	none	100:0	1.9	21.7	1339	13.84	OPP
18	Z6020	phenol	70:30	2.4	149	1302	122.3	OPP
19	Z6020	2-naphthol	70:30	3.1	39.4	102	40.7	105.1

where:

- 1: OTR is oxygen transmission rate or oxygen gas permeability
- 2: $OTR_{predicted}$ was calculated by the use of the Generic Composite Permeability Eq: $T_i/P_i = T_s/P_s + T_c/P_c$ where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_i , P_i), substrate (T_s , P_s), & coating (T_c , P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 $cc/m^2/day$ at 0%RH.
- 3: same as 2 except that the permeability was measured to be 1238 $cc/m^2/day$ as measured at 90%RH
- 4: Permeability expected is that provided by the base film OPP itself

In Examples 20 - 21 below, coating compositions were prepared from 1, 4 cyclohexanediol and amino functional silanes. These examples provide comparative results to demonstrate the need for phenolic compounds, as opposed to cyclic alkyl alcohols, for utility in the present invention.

Example 20 -- A1110 /1,4-cyclohexanediol (70:30wt) on OPP

A solution of 2.1 g of A1110 and 7 g of methanol was prepared and 0.9 g of 1,4-cyclohexanediol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 229.3 cc dry and >1000 cc wet and the coating thickness was found to be 1.8 micrometers.

Example 21 -- Z6020 /1,4-cyclohexanediol (70:30wt) on OPP

A solution of 2.1 g of Z6020 and 7 g of methanol was prepared and 0.9 g of 1,4-cyclohexanediol was added with stirring. This was coated on the substrate after 1 hour of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 261.7 cc dry and 1303.3 cc wet and the coating thickness was found to be 1.27 micrometers.

The results, shown in Table 5, demonstrate that coating compositions based on amino functional silanes and cyclic alkyl alcohols do not provide useful barrier properties.

Table 5

Barrier Data: Examples 20-21 (amino functional silanes + 1,4-cyclohexanediol)

Example #	Silane	phenol type	Ratio silane/phenol	Thickness	OTR ¹ 0%RH	OTR 90%RH	OTR ² predicted 3micrometers coating 0%RH	OTR ³ predicted 3micrometers coating 90%RH
			wt	μ	cc/m ² /day	cc/m ² /day	cc/m ² /day	cc/m ² /day
OPP	-	-	-	-	1191	1238	-	-
1	A1110	none	100:0	1.2	63.1	1253	26.1	OPP ⁴
20	A1110	1,4-CHD ⁵	70:30	1.8	229.3	> 1000	149.1	OPP
2	Z6020	none	100:0	1.9	21.7	1339	13.84	OPP
21	Z6020	1,4-CHD	70:30	1.27	261.7	1303.3	268.5	OPP

where:

1: OTR is oxygen transmission rate or oxygen gas permeability

2: OTR_{predicted} was calculated by the use of the Generic Composite Permeability Eq: $T_i/P_i = T_s/P_s +$

T_c/P_c where **T** refers to the thickness, in micrometers, and **P** to the permeability coefficient of the

composite (T_t , P_t), substrate (T_s , P_s), & coating (T_c , P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 cc/m²/day at 0%RH.

- 3: same as 2 except that the permeability was measured to be 1238cc/m²/day as measured at 90%RH
- 4: Permeability expected is that provided by the base film OPP itself
- 5: 1,4-CHD is 1,4-cyclohexane diol

Examples 22-24 were conducted to further demonstrate the unexpected improvements in barrier properties obtained for the reaction product species from amino functional silanes with phenolic compounds. In Examples 22-24, pyrogallol was added to pentaerythritol tetraacrylate (PETA) in the weight ratios as indicated. Pyrogallol is a solid, and cannot be cast into a film alone. Thus, the pyrogallol had to be cast via a coating matrix that would not react or interact with the pyrogallol. An acrylate coating composition was prepared from pentaerythritol tetraacrylate (PETA, SR 295) with and without pyrogallol, and cured with a photoinitiator (Darocur 1173 from CIBA additives) on OPP, for this purpose.

Example 22 -- PETA alone on OPP

A solution of 3 g of PETA and 7 g of methanol was prepared and 0.1 g of Darocur 1173 was added 5 minutes prior to coating with stirring. This was coated on the substrate after 30 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 449 cc dry and 161.2 cc wet and the coating thickness was found to be 3.6micrometers..

Example 23 -- PETA/pyrogallol (90:10wt) on OPP

A solution of 2.7 g of PETA and 7 g of methanol was prepared and 0.3 g pyrogallol was added with stirring. After 1 hour , 0.1 g of Darocur 1173 was added and the mixture was coated on the substrate after an additional 30 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 1164 cc dry and 348 cc wet and the coating thickness was found to be 0.93 micrometers.

Example 24 -- PETA/pyrogallol (70:30wt) on OPP

A solution of 2.1 g of PETA and 7 g of methanol was prepared and 0.9 g pyrogallol was added with stirring. After 1 hour , 0.1 g of Darocur 1173 was added and the mixture was coated on the substrate after an additional 30 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 553.7 cc dry and 912.5 cc wet and the coating thickness was found to be 4.7 micrometers..

The results of Examples 22-24, shown in Table 6, clearly demonstrate that pyrogallol alone does not barrier properties of organic polymer films.

Table 6

Barrier Data: Examples 22-24 (acrylate + pyrogallol) on OPP

Example #	Acrylate	phenol type	Ratio acrylate/phenol wt	Thickness μ	OTR ¹ 0%RH cc/m ² /day	OTR 90%RH cc/m ² /day	OTR ² _{predicted} 3micrometers coating 0%RH cc/m ² /day	OTR ³ _{predicted} 3micrometers coating 90%RH cc/m ² /day
OPP	-	-	-	-	1191	1238	-	-
22	PETA	none	100:0	3.6	449	161.2	507.4	192.1
23	PETA	Pyrogallol	90:10	0.93	1164	348	1108.7	133.8
24	PETA	Pyrogallol	70:30	4.7	553.7	912.5	687.8	1009

where:

1: OTR is oxygen transmission rate or oxygen gas permeability

2: $OTR_{predicted}$ was calculated by the use of the Generic Composite Permeability Eq: $T_t/P_t = T_s/P_s + T_c/P_c$ where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_t, P_t), substrate (T_s, P_s), & coating (T_c, P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 cc/m²/day at 0%RH.

3: same as 2 except that the permeability was measured to be 1238cc/m²/day as measured at 90%RH

In Examples 25-29, pyrogallol was added to various non-amine functional silanes in the weight ratios as indicated. These experiments were conducted as controls to show the necessity of using an amino functional silane to create the compositions of the present invention. All non-amine functional silanes used were commercial products of Dow Corning Corporation.

Example 25 -- glycidoxypropyltrimethoxy silane/pyrogallol (70:30 wt) on OPP

A solution of 2.1 g of glycidoxypropyltrimethoxy silane and 7 g of methanol was prepared and 0.9 g of pyrogallol was added with stirring. After 20 minutes, 0.2g of Tyzor DC was added. This mixture was coated on the substrate after 10 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 77.7 cc dry and 848 cc wet and the coating thickness was found to be 3.3 micrometers.

Example 26 -- methyltrimethoxy silane/pyrogallol (70:30 wt) on OPP

A solution of 2.1 g of methyltrimethoxy silane and 7 g of methanol was prepared and 0.9 g of pyrogallol was added with stirring. After 20 minutes, 0.2 g of Tyzor DC was added. This mixture was coated on the substrate after 10 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 1197.9 cc dry and 1322 cc wet and the coating thickness was found to be 0.9 micrometers.

Example 27 -- bis(trimethoxysilyl)ethyl)benzene /pyrogallol (70:30 wt) on OPP

A solution of 2.1 g of bis(trimethoxysilylethyl)benzene and 7 g of methanol was prepared and 0.9 g of pyrogallol was added with stirring. After 20 minutes, 0.2 g of Tyzor DC was added. This mixture was coated on the substrate after 10 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 844.2 cc dry and 1104 cc wet and the coating thickness was found to be 1.8 micrometers.

Example 28 -- vinyltrimethoxy silane/pyrogallol (70:30 wt) on OPP

A solution of 2.1 g of vinyltrimethoxy silane and 7 g of methanol was prepared and 0.9g of pyrogallol was added with stirring. After 20 minutes, 0.2 g of Tyzor DC was added. This mixture was coated on the substrate after 10 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 1279 cc dry and in excess of 1000 cc wet and the coating thickness was found to be 0.9 micrometers.

Example 29 -- isobutyltrimethoxy silane/pyrogallol (70:30 wt) on OPP

A solution of 2.1 g of isobutyltrimethoxy silane and 7 g of methanol was prepared and 0.9g of pyrogallol was then added with stirring. After 20 minutes, 0.2 g of Tyzor DC was added. This mixture was coated on the substrate after 10 minutes of mixing by the use of a # 18 drawdown rod. After coating, drying and curing, the permeability was determined to be 1255 cc dry and in excess of 1000 cc wet and the coating thickness was found to be 2.5 micrometers.

The use of non amine functional silane with phenolic compounds did not produce suitable barrier coatings, as shown in Table 7.

Table 7

Barrier Data: Examples 25-29 (non-amino functional silanes + pyrogallol) on OPP

Example #	silane	phenol	Ratio silane/phenol	Thickness	OTR ¹ 0%RH	OTR 90%RH	OTR ² predicted ² 3micrometers coating 0%RH	OTR ³ predicted ³ 3micrometers coating 90%RH
			wt	μ	cc/m ² /day	cc/m ² /day	cc/m ² /day	cc/m ² /day
OPP	-	-	-	-	1191	1238	-	-
3	A1170	pyrogallol	90:10	3.6	2.3	0.67	2.8	0.8
25	GTMS ⁴	pyrogallol	70:30	3.3	77.7	848	84.9	873
26	MTM ⁵	pyrogallol	70:30	0.9	1198	1322	OPP ⁹	OPP
27	bTMS ⁶	pyrogallol	70:30	1.8	844	1104	707	1029
28	VTMS ⁷	pyrogallol	70:30	0.9	1279	> 1000	OPP	OPP
29	iBTM ⁸	pyrogallol	70:30	2.5	1255	> 1000	OPP	OPP

where:

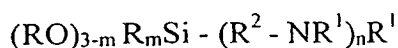
- 1: OTR is oxygen transmission rate or oxygen gas permeability
- 2: $OTR_{predicted}$ was calculated by the use of the Generic Composite Permeability Eq: $T_l/P_l = T_s/P_s + T_c/P_c$ where T refers to the thickness, in micrometers, and P to the permeability coefficient of the composite (T_l, P_l), substrate (T_s, P_s), & coating (T_c, P_c). The substrate OPP was measured to be 30 micrometers thick and have an OTR of 1191 cc/m²/day at 0%RH.
- 3: same as 2 except that the permeability was measured to be 1238cc/m²/day as measured at 90%RH
- 4: GTMS is glycidoxypopyltrimethoxy silane
- 5: MTMS is methyltrimethoxy silane
- 6: bTMSB is bis(trimethoxysilylethyl)benzene
- 7: VTMS is vinyltrimethoxy silane
- 8: iBTMS is isobutyltrimethoxy silane
- 9: Permeability expected is that provided by the base film OPP itself

Other variations may be made in compounds, compositions, and methods described herein without departing from the essential features of the invention. The embodiments of the invention specifically illustrated herein are exemplary only and not intended as limitations on their scope except as defined in the appended claims.

Claims:

1. A composition comprising a reaction product of :

(A) an amino functional silane having the formula,



wherein m is 0, 1 or 2, n is 1 - 3,

R is independently a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms,

R¹ is independently a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an arylalkyl group, an acryl group, a methacryl group, or an alkylaryl group,

R² is independently selected from the group consisting of,

linear or branched alkylene groups having from 1 to 12 carbon atoms,

arylene groups having from 6 to 12 carbon atoms,

and linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or polyether group, and

(B) a phenolic compound,

wherein said reaction product is free of phenol-formaldehyde resole resin.

2. The composition of claim 1 wherein said phenolic compound has substituents independently selected from the group consisting of hydrogen, alkyl, aryl, hydroxy, carboxylic acids, esters, thio, amino, amide, and nitro.

3. The composition of claim 2 wherein said phenolic compound comprises a mono aromatic ring structure having two or more hydroxy group substituents.

4. The composition of claim 3 wherein said phenolic compound is pyrogallol.

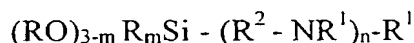
5. The composition of claim 2 wherein said phenolic compound comprises a polycyclic aromatic ring structure selected from the group consisting of naphthyl, anthryl, and phenanthryl aromatic derivatives.

6. The composition of claim 1, wherein the amino functional silane is trimethoxysilylpropylamine or N-(2-amino ethyl)gamma aminopropyl trimethoxysilane.

7. The composition of claim 1, wherein the reaction product is dissolved in a solvent in an amount of 1-99% and the solvent constitutes 60-95 parts by weight of the total composition.

8. A method for preparing a substrate with improved barrier properties comprising coating the substrate with a composition comprising the reaction product of;

(A) an amino functional silane having the formula,



wherein m is 0, 1 or 2, n is 1 - 3,

R is independently a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms,

R^1 is independently a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an arylalkyl group, an acryl group, a methacryl group, or an alkylaryl group,

R^2 is independently selected from the group consisting of,

linear or branched alkylene groups having from 1 to 12 carbon atoms,

arylene groups having from 6 to 12 carbon atoms,

and linear or branched hydrocarbon groups having from 1 to 16 carbon

atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or polyether group, and

(B) a phenolic compound,

and curing the composition on the substrate.

9. The method of claim 8, wherein the substrate is selected from the group consisting of polyolefins; oriented polypropylene; cast polypropylene; polyethylene and polyethylene copolymer; polystyrene; polyesters; polyethylene terephthalate; polyethylene naphthalate; polyolefin copolymers; ethylene vinyl acetate; ethylene acrylic acid; ethylene vinyl alcohol; polyvinylalcohol and copolymers thereof; polyamides, nylon; and nylon MXD6; polyimides; polyacrylonitrile; polyvinylchloride; polyvinyl dichloride; polyvinylidene chloride; polyacrylates; ionomers; polysaccharides; regenerated cellulose; silicone; rubbers and sealants; natural and synthetic rubbers; glassine and clay coated paper; paper board; craft paper; metallized films; and vapor deposited metal oxide coated polymer films.

10. The method of claim 8, wherein the composition is disposed on one or more additional substrates to form a laminate.

11. The method of claim 10, wherein the additional substrates used to form the laminate are selected from the group consisting of polyolefins; oriented polypropylene; cast polypropylene; polyethylene and polyethylene copolymer; polystyrene; polyesters; polyethylene terephthalate; polyethylene naphthalate; polyolefin copolymers; ethylene vinyl acetate; ethylene acrylic acid; ethylene vinyl alcohol; polyvinylalcohol and copolymers thereof; polyamides, nylon; and nylon MXD6; polyimides; polyacrylonitrile; polyvinylchloride; polyvinyl dichloride; polyvinylidene chloride; polyacrylates; ionomers; polysaccharides; regenerated cellulose; silicone; rubbers and sealants; natural and synthetic rubbers; glassine and clay coated paper; paper board; craft paper; metallized films; and vapor deposited metal oxide coated polymer films.

12. The method of claim 8, wherein the substrate is treated with a primer.

13. The method of claim 13, wherein the primer is selected from the group consisting of a silane, polyethylenimine, and carbodiimide.

14. The method of claim 13, wherein the additional substrate or substrates are treated with a primer.

15. A substrate with improved barrier properties as prepared by the method of claim 8, 10, or 12.

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 01/05573

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09D4/00 C09D183/08 C08J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	--- PATENT ABSTRACTS OF JAPAN vol. 1996, no. 10, 31 October 1996 (1996-10-31) & JP 08 165365 A (NIPPON SHOKUBAI CO LTD), 25 June 1996 (1996-06-25) abstract	1
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Date of the actual completion of the international search

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